

5.3 VOC/NO_x Ratios

Abstract

This section presents calculated VOC to NO_x ratios for six sites in the South Coast Air Basin. Total non-methane organic carbon (TNMOC) measured for the PAMS program was used for the VOC concentration. Hourly NO_x values were averaged to allow comparison with three-hour VOC canister samples. The late-morning (8:00 – 12:00) VOC/NO_x ratios are typically 10 to 30% higher on the weekend than on weekdays with average weekend VOC/NO_x ranging from 5.0 – 9.3 and average weekday ratios ranging from 4.4 – 7.3. However, uncertainties regarding actual VOC concentrations, as well as spatial and temporal variations in the ozone isopleths make it difficult to determine the effect on ozone concentrations of this increase in VOC/NO_x ratio from weekday to weekend.

5.3.1 Introduction

As stated in chapter 3, the chemistry involved in ozone production in a system which contains Volatile Organic Compounds (VOC) and NO_x is extremely non-linear. The ratio of VOC concentration to NO_x concentration can provide information as to the effect on the ozone concentration of changes in precursor concentrations. If the VOC/NO_x ratio is greater than approximately 6 – 9, the system is termed NO_x-limited and decreases in NO_x are expected to decrease ozone. If the VOC/NO_x ratio is less than 6 - 9, the system is termed VOC limited and decreases in NO_x are expected to increase the peak ozone concentration. However, simple two-dimensional isopleths, such as shown in Figure 3-1, encourage an overly simplistic application of VOC/NO_x ratio to predict behavior. Three-dimensional isopleths (see for example pages 883-885 in Finlayson-Pitts, 2000) provide a more complete picture of the effects of changes in precursor concentration on ozone concentration. Besides VOC and NO_x concentrations, factors which influence the shape of the isopleth include composition of the VOC and NO_x mixtures, both of which will change over time. Thus, while the VOC/NO_x ratio is a key variable, it is advisable to keep in mind the complexity, both temporally and spatially, of the chemistry in a system as large as the South Coast Air Basin (SoCAB).

5.3.2 Methodology

VOCs are not criteria pollutants and thus the amount of VOC data is much more limited than that of criteria pollutants such as NO_x and O₃. However, the Photochemical Assessment Monitoring Stations (PAMS) program requires detailed VOC measurements at a number of sites in the SoCAB. For the PAMS program several three hour-canister samples are collected every third day during July through September. The samples are analyzed for the 56 C₂ – C₁₀ target hydrocarbons by a gas chromatograph equipped with a flame ionization detector. This method is not suitable for carbonyls such as formaldehyde and acetaldehyde and a separate analysis is done for carbonyls. The VOC concentrations used in this analysis do not

include carbonyls. In addition to the individual concentrations of the specific PAMS hydrocarbons, the analysis reports total non-methane organic compounds (TNMOC) which includes other non-identified or non PAMS compounds. While some studies have indicated that the PAMS measurements underestimate the total hydrocarbon concentrations in the atmosphere by approximately 30% (Paulson, 1999), the PAMS data comprise the largest database of ambient hydrocarbon concentrations. For this reason, TNMOC from the PAMS program was used to estimate the VOC concentration in this study.

Sites in the SoCAB for which VOC data are available include Azusa, Banning, Burbank, Hawthorne, Los Angeles-North Main and Upland. While VOC data are available for a site in Pico Rivera, the data are suspect due to likely contamination from a neighboring facility and therefore were not used. VOC data for 1995 – 1998 were downloaded from EPA's AIRS database. Burbank and Hawthorne did not have VOC data for 1995 and 1996 and no TNMOC data for 1996 were available for Upland. Except for the Los Angeles-North Main site, in 1996 – 1998 3-hour canister samples were collected every third day starting at 23:00, 2:00, 5:00, 8:00, 11:00, 14:00, 17:00, and 20:00 PST. In 1995, the start time for the sampling was one hour later. Throughout 1995 – 1998, 2 three-hour samples were collected at 5:00 and 12:00 PST at the Los Angeles-North Main station. The program VOCDAT (Sonoma Technology, Inc., 1999) was used to generate files containing date, time, TNMOC, and Sum of PAMS Compounds. The Sum of PAMS Compounds as a percent of the TNMOC was calculated as a check for suspect data. Data were rejected if the Sum of PAMS Compounds was significantly greater than the TNMOC or if the Sum of PAMS Compounds represented less than 50% of the TNMOC.

Hourly average NO_x concentrations in ppm were obtained from ARB's ADAM database. The data were reported with 3 significant figures, except for Banning which reported NO_x concentrations with 2 significant figures. No QC checks were performed. To allow comparison with 3 hour canister VOC samples, an average NO_x concentration was calculated by averaging the three hourly averages. Due to daily calibration checks, NO_x data are generally not available for 4:00 - 5:00 PST. Thus, the "3-hour" average NO_x concentrations for the periods beginning at 2:00 and 3:00 are averages of 2:00 to 4:00 and 3:00 to 4:00 and 5:00 to 6:00, respectively. The data were divided into weekday (Monday – Friday) and weekend (Saturday – Sunday) data sets. For each date and time, the ratio of Total NMOC in ppbC to NO_x in ppb was calculated. The arithmetic mean, standard deviation and standard error of the ratios were calculated.

5.3.3 Results

Figures 5.3-1 – 5.3-6 show the VOC/NO_x values available for 1995 – 1998 for the six sites. The weekend data are offset by 15 minutes to display in the figures. Most of the data sets show occasional high values, however, the majority of the ratios are between 4 and 10. This supports a description of the chemistry of the region as likely being VOC-limited. Banning appears to be unusual with an average VOC/NO_x ratio closer to 3. Banning's VOC concentrations were lower than the others, with

TMNOC regularly less than 100 ppbC. Additional efforts should be made to confirm these hydrocarbon values. The average VOC/NO_x as a function of time of day is shown in Figures 5.3-7 – 5.3-12. The error bars represent one standard error. The average ratio, standard deviation and n are given in Tables 5.3-1 – 5.3-6. The weekend ratio is slightly higher than the weekday ratio during the morning at all of the sites. This increase in weekend ratio continues throughout the day, except at Azusa and Banning where the weekday ratio is slightly higher than the weekend. The percent increase of the average weekend VOC/NO_x over the average weekday VOC/NO_x is shown for all sites in Figure 5.3-13. (The 20:00 data for Banning are not shown.) Between 5:00 and 11:00 weekend ratios are typically 10 to 30% higher than weekday ratios.

This finding of higher VOC/NO_x ratios on weekends was also observed by ENVIRON (ENVIRON, 1998). For the period 1994 – 1996, ENVIRON calculated an average weekday morning VOC/NO_x ratio of approximately 9 and a weekend ratio of approximately 14 at Los Angeles-North Main. While data collected at Azusa indicated slightly lower ratios of 6 and 9 for the weekday and weekend respectively, a similar increase of approximately 50% was observed in the weekend VOC/NO_x ratio. Thus, while both this analysis and the one done by ENVIRON observed a higher VOC/NO_x ratio on the weekend, the ARB analysis observed both lower absolute values for the VOC/NO_x ratios and a smaller percent increase on the weekend. Although changes in gasoline occurred in the SoCAB in 1995, a more likely source of the discrepancy is the use of hydrocarbon data collected by different methods.

Much of the VOC data used in the ENVIRON analysis was collected by Bendix 8202 continuous Total Hydrocarbon (THC) analyzers. The regression,

$$\text{TNMHC (ppb)} = \{\text{THC (ppb)} - [1527 + 17 \cdot (\text{Year} - 1987)]\} / 1.54, \text{ (Fujita, 1995),}$$

was used to estimate total nonmethane hydrocarbon (TNMHC) concentrations from the THC data. In 1995, three hour canister VOC data were collected and analyzed by Desert Research Institute at two sites, Los Angeles-North Main and Azusa. Figure 5.3-14 shows 8202 THC data versus the canister data analyzed by GC-FID for this period. The line is the regression derived by Fujita. It is clear that, while the regression fits the Los Angeles-North Main data quite well, the Azusa data appears to be offset from the Los Angeles-North Main data.

Another possible explanation exists for the larger increase in weekend VOC/NO_x ratios observed by ENVIRON. Leon Dolislager also observed a significant difference in weekday to weekend VOC/NO_x ratios in data collected by the ARB in the 1980s. (Dolislager, 2000) These ratios were also calculated using THC data. The increase in VOC/NO_x ratio was driven by the decrease in weekend NO_x because weekend THC declined only slightly on the weekend, with the weekend THC equal to approximately 90% of the weekday THC. This observation is very similar to ENVIRON's observation of a 20% and 10% difference in THC in 1986-1989 and 1994-1996 respectively. TMNOC from the PAMS data, as seen in Table 5.3-7 and Figure 5.3-14, appears to observe weekday VOC concentrations that are 20 to 50%

higher than the weekend VOC concentrations. If all of these observations are accurate, it implies there is a difference in the VOC inventory such that on the weekend there is an increase in compounds not measured by the PAMS but which are measured by THC measurements. Professor Paulson at UCLA has developed an instrument which collects simultaneous measurements of TNMOC and PAMS speciated data. Her results (Paulson, 1999) indicate that PAMS data underestimates hydrocarbon concentrations by approximately 30% overall. Examination of her ambient data may indicate if the ratio of PAMS hydrocarbons to TNMOC displays a weekend effect.

5.3.4 Conclusions

In general, VOC/NO_x ratios calculated using TNMOC from PAMS data range between 4 and 9, with weekend ratios 10 to 30% higher than weekday ratio at the same site and time. These numbers indicate that the ozone chemistry in the SoCAB is likely VOC limited and appears to support the NO_x-Reduction hypothesis. However, this conclusion should be regarded as tentative for a number of reasons. Actual hydrocarbon concentrations may be as much as 30% greater than those used in this analysis. This would result in VOC/NO_x ratios that are also 30% greater. Also, the difference in the relative weekday to weekend change in THC data versus PAMS data indicates there may be a difference in the VOC composition on the weekend versus the weekdays. The composition of the mixture represented by NO_x also changes on the weekend. For example, section 5.1 found that NO₂/NO ratios are generally higher on early Sunday morning. Thus, it would be unwise to predict the effect of a 10 to 30% change in the VOC/NO_x without a more thorough understanding of the shapes of isopleths appropriate for each site and time.

5.3.5 Recommendation

- 1) PAMS data provides only 3-hour average VOC concentrations every third day. To more accurately characterize the diurnal variations in VOC/NO_x ratios, hourly total VOC measurements should be collected at three sites in the SoCAB for at least 18 months. The study should include two ozone seasons to lessen the impact of unusual meteorology.
- 2) VOC concentrations estimated from PAMS data underestimate actual VOC concentrations. If the missing fraction is assumed to be a fixed percentage, this underestimation would not change the percent change in weekend VOC/NO_x ratios but would increase the absolute VOC/NO_x ratio. For this reason VOC/NO_x should be recalculated to include carbonyls and/or an increase of approximately 30% in VOC concentrations.
- 3) An investigation of the possible differences in between THC and Total NMOC from the PAMS analysis should be undertaken as this may support the hypothesis that weekend emissions of VOC may be different in some way due to weekend activities.

5.3.6 References

ENVIRON International Corporation, (1998) "Analysis of Weekend-Weekday Differences in Ozone and Ozone Precursors in the South Coast (Los Angeles) Air Basin" Prepared for American Automobile Manufacturers Association.

Dolislager, Leon, personal communication.

Finlayson-Pitts, B. J., J. N. Pitts, Jr, (2000) "Chemistry of the Upper and Lower Atmosphere", Academic Press.

Fujita, Eric M. (1995) "Ambient Versus Emission Inventory NMHC, CO, NO_x Trends in the South Coast Air Basin (1987-1993). Paper 95-RP113B.01, presented at the Air & Waste Management Association 88th Annual Meeting, San Antonio, TX, 18-23 June 1995.

Paulson, S. (1999) "Total Non-Methane Organic Carbon Development and Validation of a New Instrument and Measurements of Total Non-Methane Organic Carbon and C₂-C₁₀ Hydrocarbons in the South Coast Air Basin", ARB Contract No. 95-335.

Table 5.3-1**Azusa 1995 - 1998**

Year	Time	Weekday			Weekend		
		Average	Stdev	N	Average	Stdev	N
1995	0:00	6.44	2.10	15	6.37	0.98	7
1996-1998	2:00	6.89	2.44	51	8.24	2.87	21
1995	3:00	5.09	1.16	13	6.70	0.89	7
1996-1998	5:00	5.99	2.41	54	7.49	2.79	22
1995	6:00	4.50	0.87	14	4.45	1.49	7
1996-1998	8:00	5.36	2.21	55	6.63	2.26	22
1995	9:00	4.60	0.90	13	5.03	2.14	7
1996-1998	11:00	6.32	2.20	52	7.35	2.61	21
1995	12:00	5.81	1.62	14	6.29	1.96	7
1996-1998	14:00	6.51	2.65	54	6.95	1.94	18
1995	15:00	6.35	2.09	13	5.37	0.76	6
1996-1998	17:00	5.99	2.61	51	6.63	2.42	19
1995	18:00	5.59	1.30	14	5.15	0.74	6
1996-1998	20:00	5.86	2.57	52	5.86	2.06	20
1995	21:00	5.35	1.45	14	5.08	0.50	6
1996-1998	23:00	7.21	3.13	53	6.66	1.56	18

Table 5.3-2**Banning 1997 – 1998**

Time	Weekday			Weekend		
	Average	Stdev	N	Average	Stdev	N
2:00	2.17	1.10	30	2.65	1.19	9
5:00	2.43	0.75	28	2.97	2.17	10
8:00	4.46	6.23	25	4.99	5.62	10
11:00	3.71	3.35	22	2.80	1.66	6
14:00	3.25	3.10	22	2.21	0.85	8
17:00	3.29	2.18	23	2.56	1.49	9
20:00 ^a	2.89	1.14	10	7.73	7.73	4
23:00	2.55	1.39	21	4.00	2.16	9

a 20:00 data is from 1997 only.

Table 5.3-3**Burbank 1998 (+ 9 days in 1997)**

Time	Weekday			Weekend		
	Average	Stdev	N	Average	Stdev	N
2:00	6.81	1.67	60	7.08	1.25	27
5:00	5.69	1.04	60	6.68	0.96	26
8:00	6.49	1.66	56	7.25	1.73	25
11:00	7.63	1.44	62	9.26	2.93	27
14:00	8.53	5.78	61	7.96	1.52	24
17:00	6.53	1.14	64	6.69	0.93	27
20:00	5.78	1.41	64	6.55	1.51	27
23:00	5.89	1.73	63	6.40	2.04	25

Table 5.3-4**Hawthorne 1997 – 1998**

Time	Weekday			Weekend		
	Average	Stdev	N	Average	Stdev	N
2:00	7.29	3.08	21	8.07	5.32	8
5:00	5.53	3.10	29	7.06	3.11	10
8:00	7.33	2.09	24	9.30	5.71	10
11:00	8.66	3.65	21	10.55	3.22	10
14:00	6.27	3.26	17	7.51	3.00	7
17:00	9.19	9.64	15	9.29	6.83	5
20:00	7.13	4.04	12	5.79	1.76	4
23:00	6.24	2.02	19	8.65	4.44	6

Table 5.3-5**Los Angeles, North Main 1995 – 1998**

Time	Weekday			Weekend		
	Average	Stdev	N	Average	Stdev	N
5:00	3.59	1.28	64	4.85	1.30	26
12:00	6.91	2.98	66	7.65	2.90	25

Table 5.3-6**Upland 1995, 1997, 1998**

Year	Time	Weekday			Weekend		
		Average	Stdev	N	Average	Stdev	N
1995	0:00	8.26	2.73	15	7.94	1.69	9
1996-1998	2:00	8.15	2.66	42	7.85	3.34	12
1995	3:00	5.91	2.64	15	7.71	1.75	9
1996-1998	5:00	4.63	1.23	40	7.13	2.12	12
1995	6:00	4.39	0.88	15	5.06	0.91	9
1996-1998	8:00	4.37	1.22	43	5.72	2.19	11
1995	9:00	4.01	0.99	15	5.38	2.22	9
1996-1998	11:00	4.97	1.86	36	6.33	2.19	12
1995	12:00	4.15	1.53	13	4.80	0.79	8
1996-1998	14:00	5.24	1.27	40	7.07	2.91	10
1995	15:00	3.62	1.01	15	5.02	1.60	7
1996-1998	17:00	5.21	2.35	43	5.32	2.39	10
1995	18:00	4.78	1.65	14	5.51	1.32	7
1996-1998	20:00	5.25	1.53	39	5.92	2.64	12
1995	21:00	5.96	1.64	14	6.98	0.71	7
1996-1998	23:00	6.95	1.79	34	7.70	2.22	14

Table 5.3-7**Average Weekday TNMOC/Weekend TNMOC**

Time	Azusa	Banning	Burbank	Hawthorne	North Main	Upland
5:00	1.30	1.54	1.08	1.34	1.28	1.48
6:00	1.51					1.35
8:00	1.40	1.06	1.33	1.00		1.38
9:00	1.45					1.06
11:00	1.41	2.02	1.20	1.11		1.36
12:00	1.39				1.23	1.29

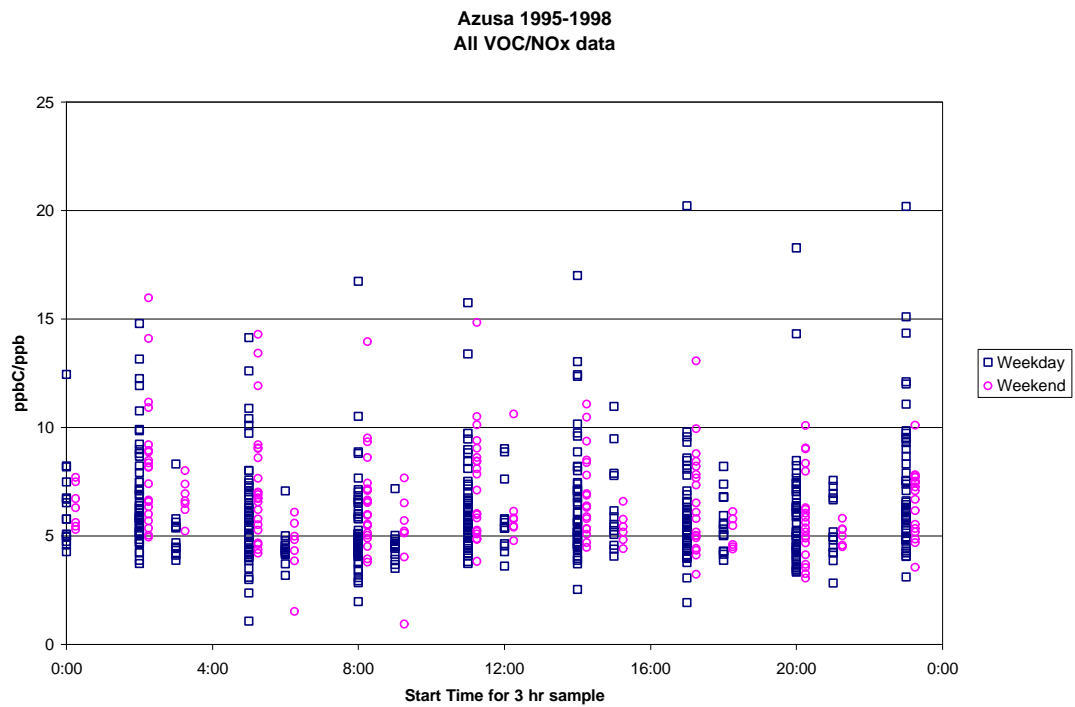
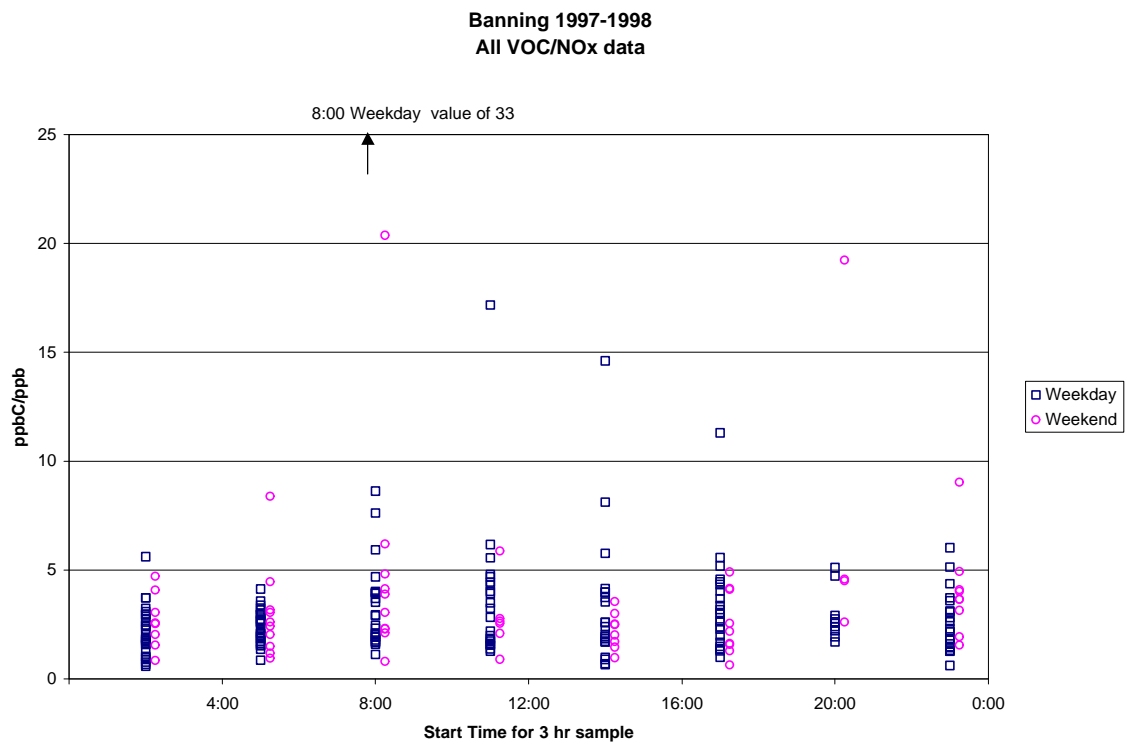
Figure 5.3-1**Figure 5.3-2**

Figure 5.3-3

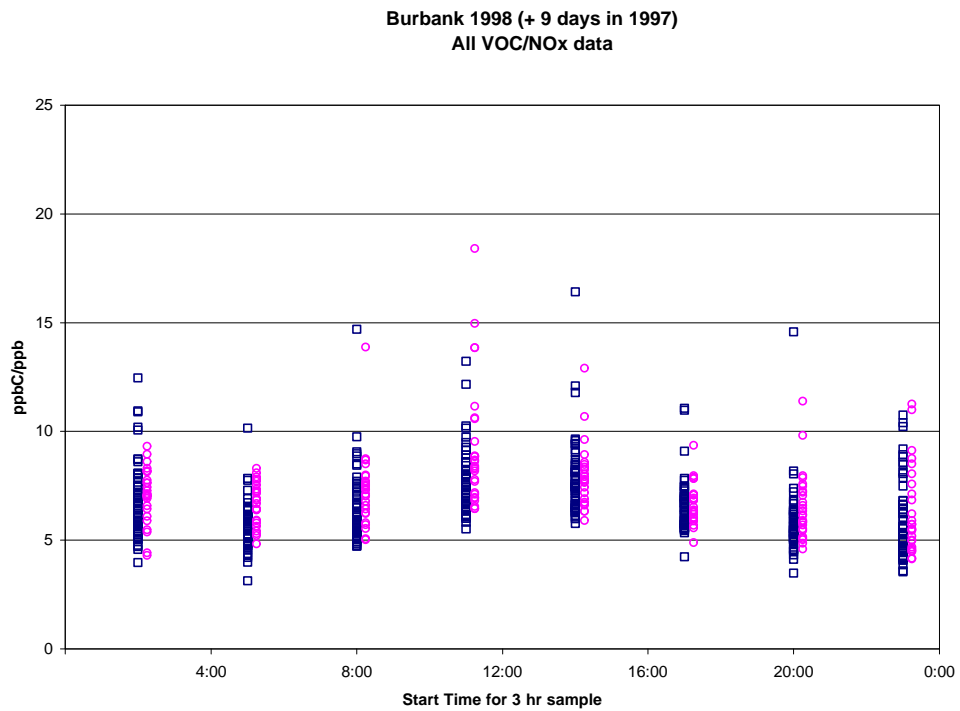


Figure 5.3-4

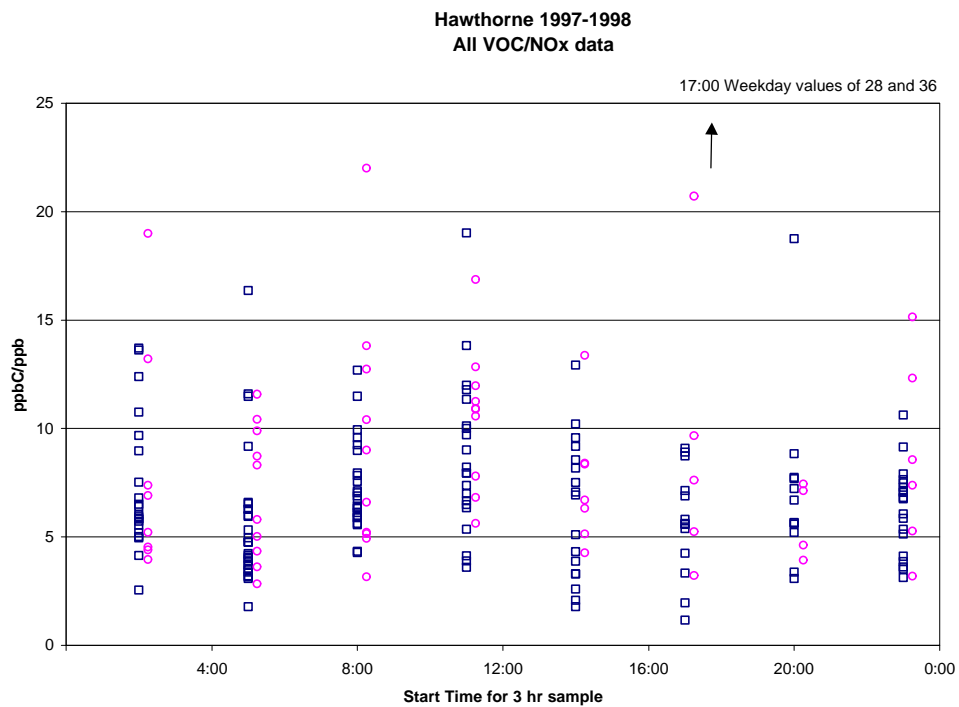


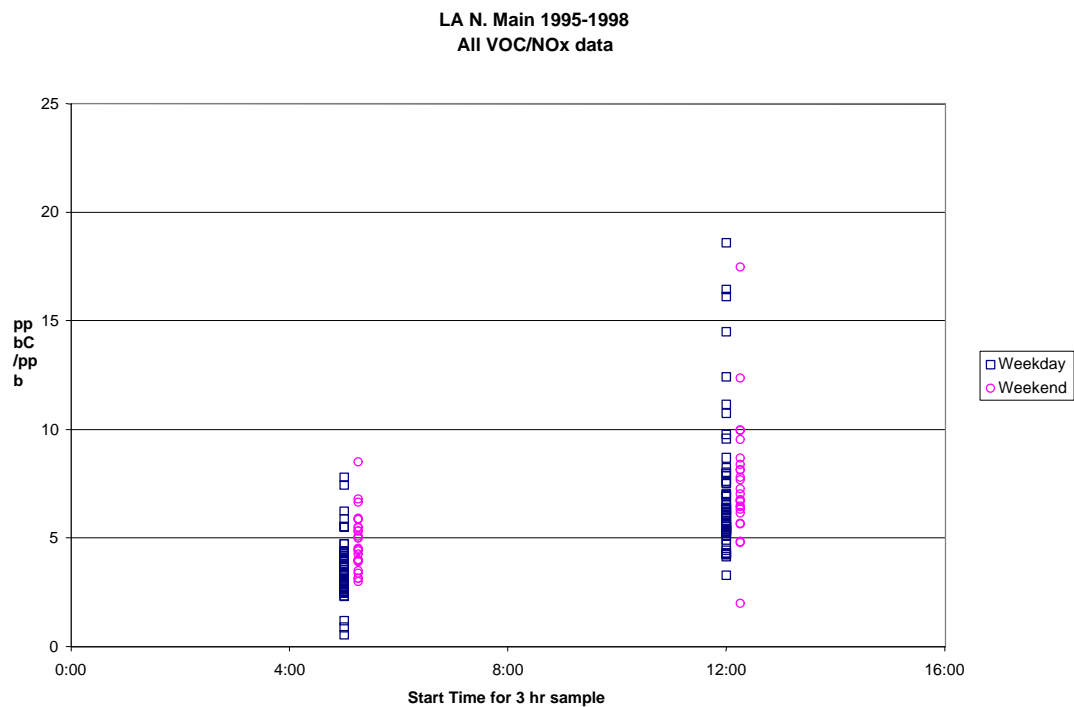
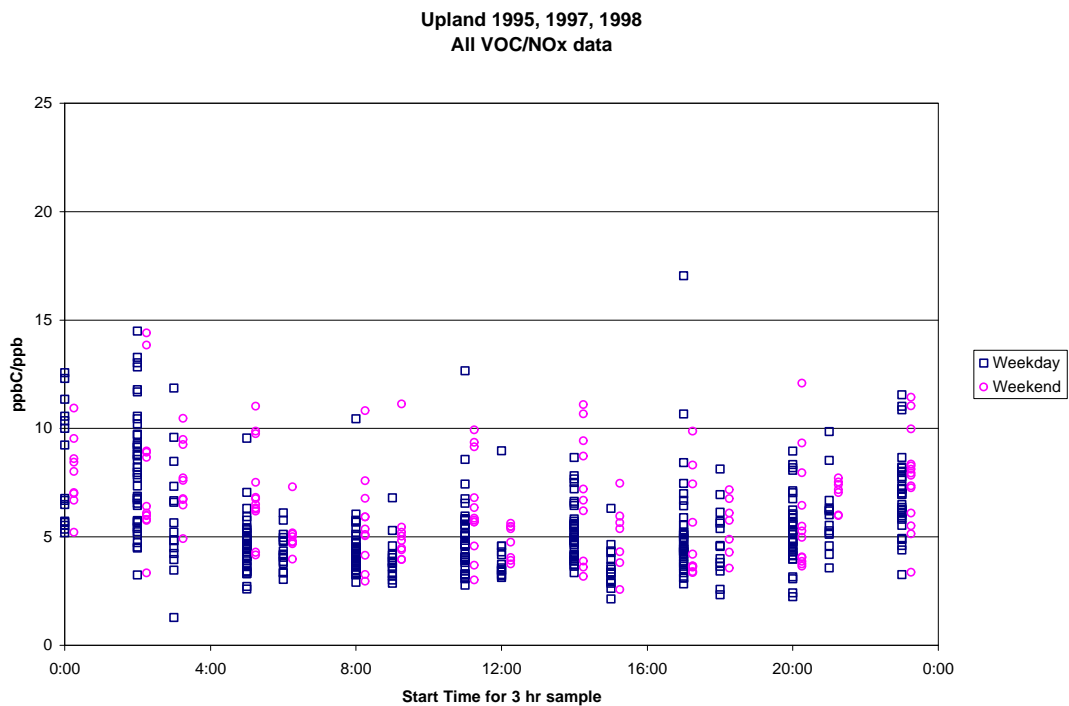
Figure 5.3-5**Figure 5.3-6**

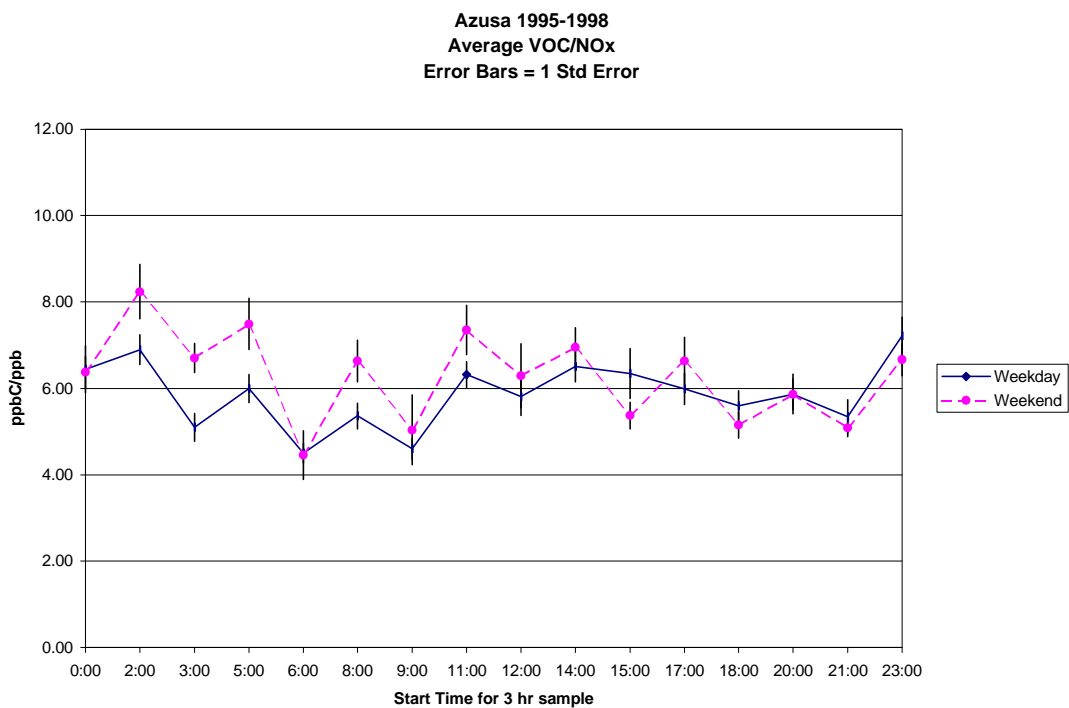
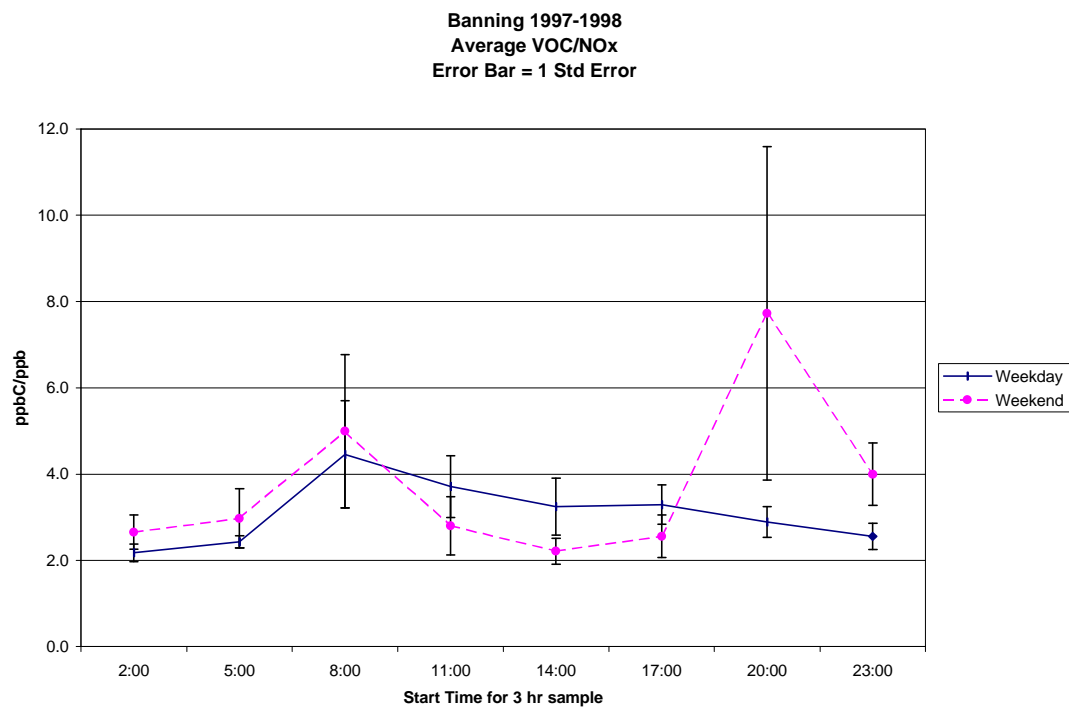
Figure 5.3-7**Figure 5.3-8**

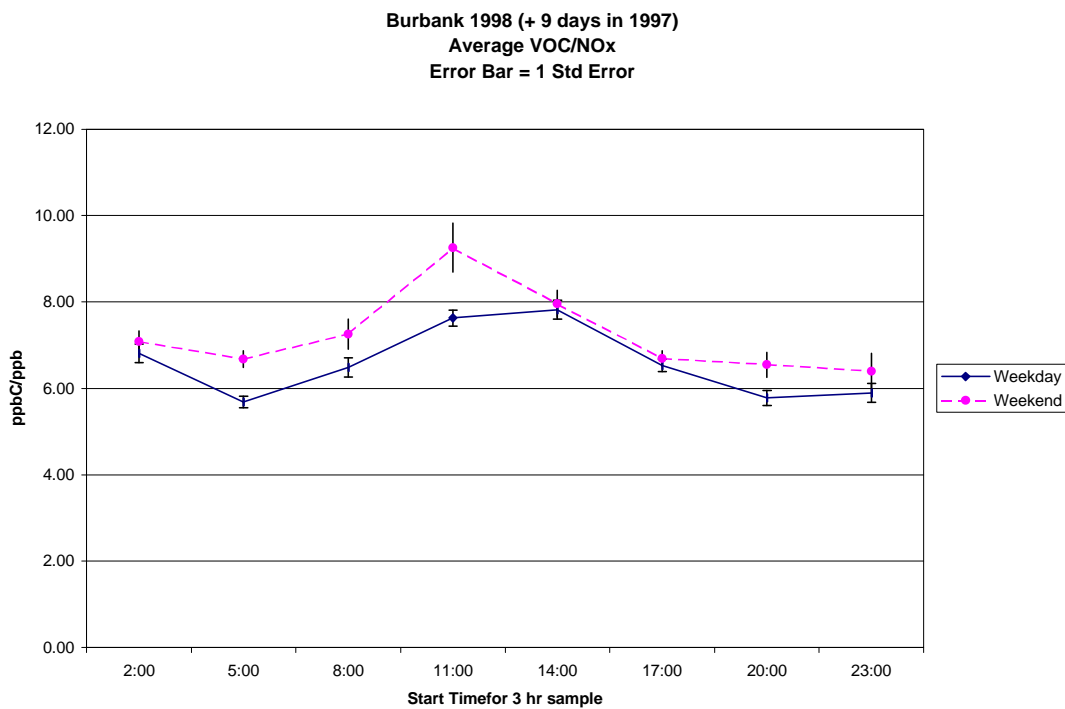
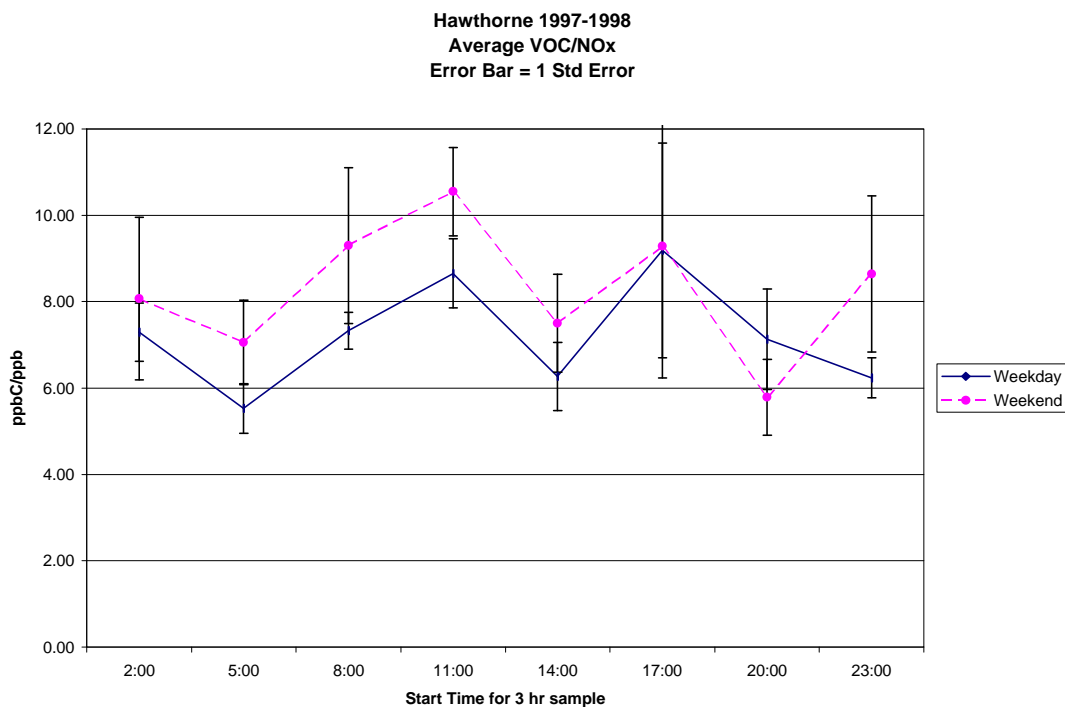
Figure 5.3-9**Figure 5.3-10**

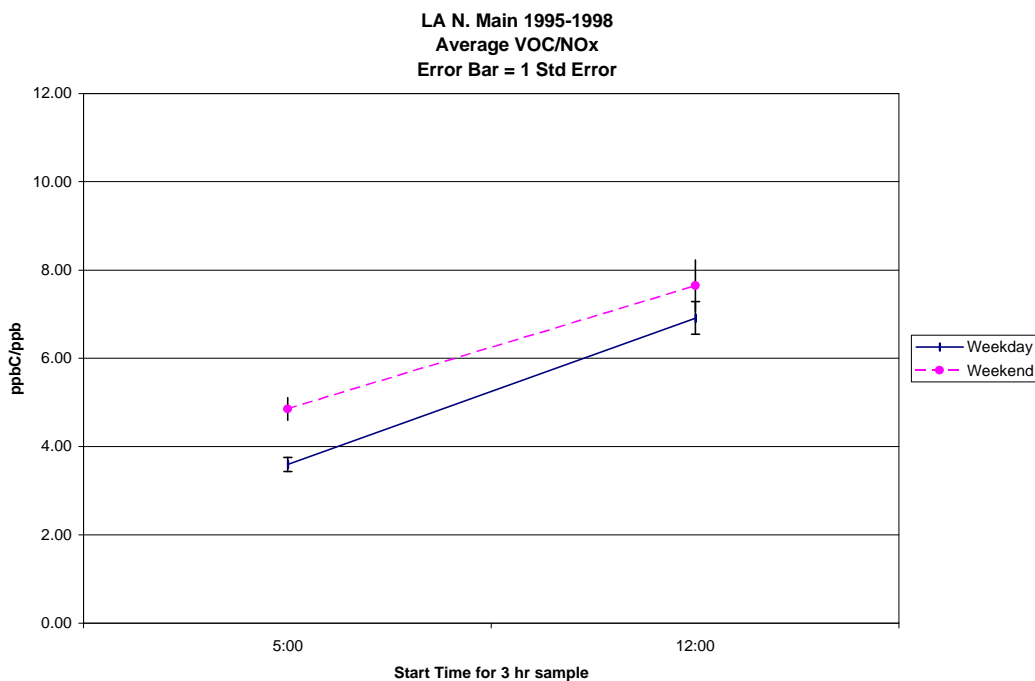
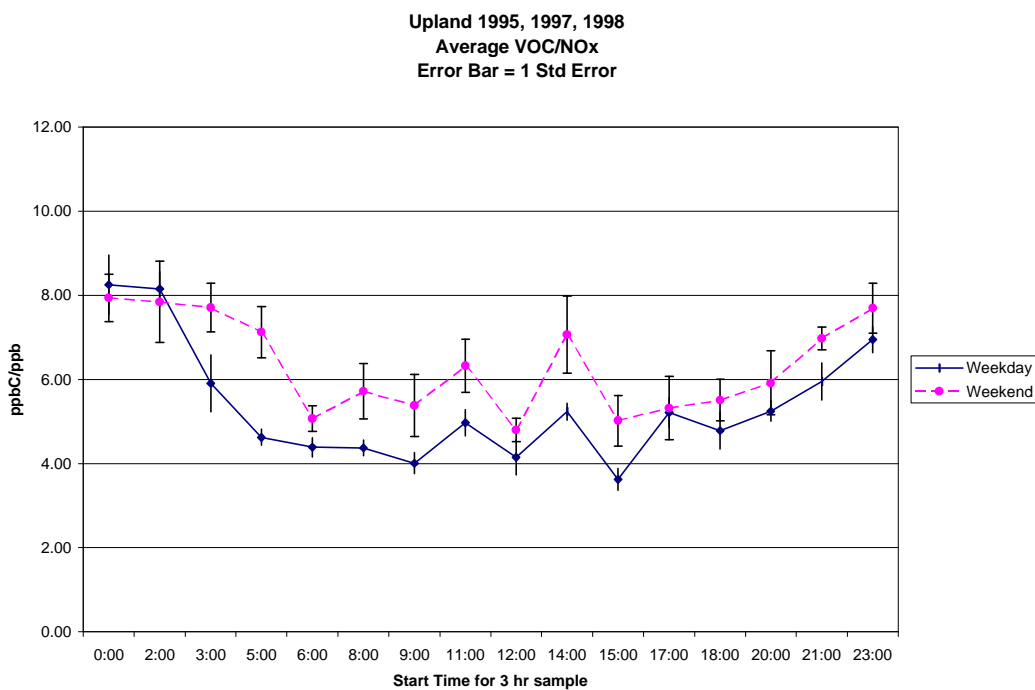
Figure 5.3-11**Figure 5.3-12**

Figure 5.3-13

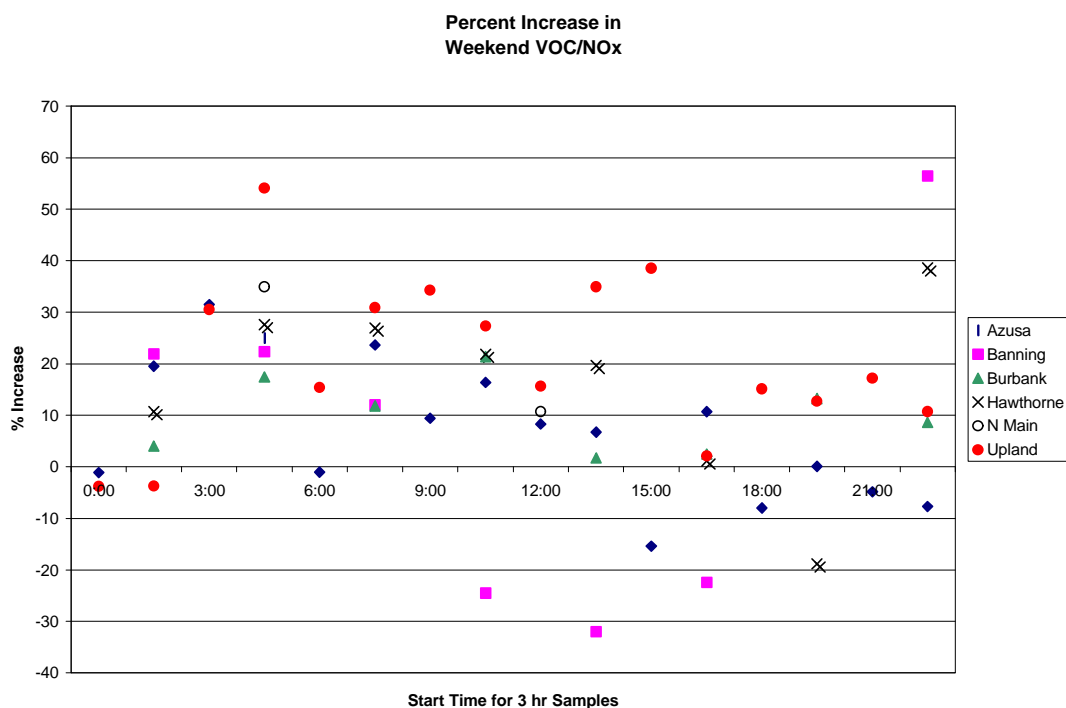


Figure 5.3-14

8202 THC vs Canister NMOC 1995 Morning Data

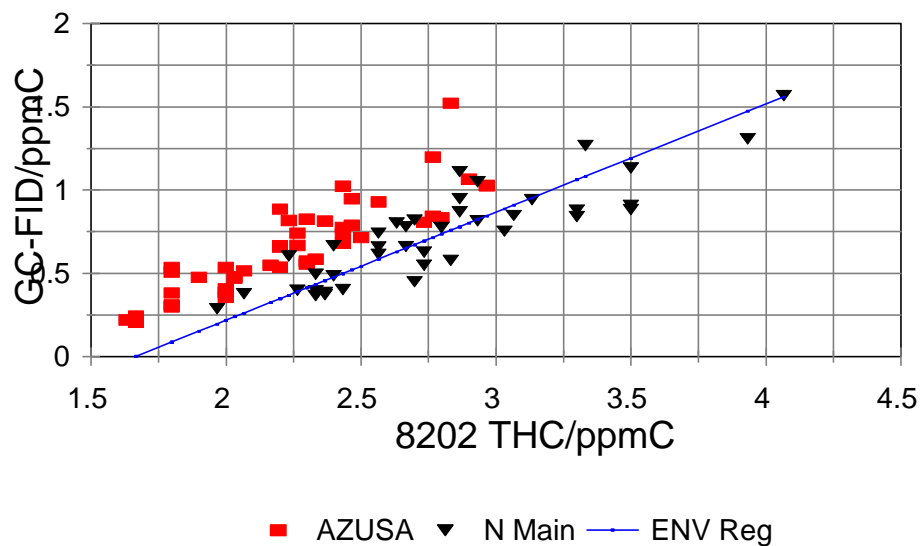


Figure 5.3-15